Summary
Perchlorate Monitoring of Water Supplies
In Suffolk County, NY

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Introduction

Perchlorate (ClO_4^-) is an anion (negatively charged ion) which is found in the environment when solid salts of perchlorate dissolve in water. The most common of these salts are ammonium, potassium and sodium perchlorate. Perchlorate is known to be extremely soluble in water, with solubility similar to common table salt. The perchlorate ion is extremely mobile in groundwater environments and can persist for very long periods of time in groundwater and surface waters due to the strong chloride-oxygen chemical bond. The ion is non-volatile, and is a strong oxidizer.

Ammonium perchlorate is used as the oxidizer and primary ingredient in solid fuel rockets – a use that dates back to World War II and is most notable in the two solid fuel rockets utilized in each space shuttle launch. It is also used in the manufacture of fireworks, certain munitions, air bag inflator charges and matches, and in analytical chemistry.

Other perchlorate compounds are used in the nuclear reactor industry (perchloric acid, $ClHO_4$), electronic tubes, lubricating oil additives, tanning and finishing leather, color fixers in fabric and dyes, electroplating, rubber manufacturing, paints and enamels. As discussed later, perchlorate is an impurity in chemical fertilizers and agricultural chemical compounds, and is a possible impurity in other salts. Perchloric acid and its salts are also reported as being used in oxygen generating systems and certain medical applications. Historically, the use of potassium perchlorate in the treatment of Graves' Disease (hyperthyroidism) is the basis for most human health effects data.

Monitoring History / Experiences Elsewhere

The first reports of perchlorate as a groundwater contaminant that could potentially be of concern followed the development of an analytical procedure to detect perchlorate at low (part per billion) concentrations in early 1997. This ion chromatography (IC) method was developed jointly by the State of California, aerospace contractors, and the US Air Force Research Lab. In a study published in the October 1999 issue of *Journal AWWA,* California researchers demonstrated that the method could reliably detect 5 ppb of perchlorate in the presence of 1000 ppm of bicarbonate, chloride or sulfate – the most common interfering substances.

The first reported detections of perchlorate as a groundwater contaminant were in samples collected at the Aerojet General Federal Superfund site in Sacramento County, California. To date, some 12 sites have been isolated in California in which solid fuel manufacturing, rocket testing, or the practice of salvaging solid fuel rocket casings by washing out weakened solid fuels, have contributed to groundwater and/or drinking water well contamination. Significant contamination findings in Nevada, Utah, Texas, Arizona, and southwestern Native American Tribal areas, have also been reported. Research by the National Aeronautics and Space Administration, the Department of Defense, and the

response to a request for information made to manufacturers by the Environmental Protection Agency, have confirmed perchlorate shipment to nearly every state.

In California, an ongoing statewide public water-monitoring program has indicated perchlorate in approximately 14% of public water systems, and 184 of 2,161 sources, with concentrations of up to 280 ppb in active wells, and 325 ppb in one inactive well. Concentrations in groundwater plumes have been reported as high as 3.7 million ppb in a monitoring well in Henderson, Nevada. Approximately 9 ppb has been reported in the Colorado River, which is the water supply source for tens of millions of people in southern California, Arizona and Nevada. The Colorado River contamination is reportedly associated with ammonium perchlorate manufacturing in Nevada. Perchlorate has also been encountered in Lake Mead at the water intake for the City of Las Vegas, with concentrations encountered between 4 and 16 ppb. The EPA reports contamination from industrial sources such as: propellant testing, explosives and ordnance manufacturing, research and disposal, rocket manufacturing and research, chemical manufacturing, agricultural chemicals manufacturing and fireworks manufacturing.

In a recently published study (*January 2001, Journal American Waterworks Association*) the American Waterworks Service Company – geographically the most diverse private water company in the US – reported perchlorate analytical results for 367 of its surface and groundwater source sites in 17 states. Perchlorate detection (greater than 4 ppb) was reported at 18 sites in 5 states (CA, IN, IA, NM, PA), with concentrations confirmed to 7.1 ppb. Many of the positive results were negative in confirmatory samples. This study reflects samples collected in 1997 and 1998.

The American Waterworks Research Foundation is independently conducting its own study of samples collected throughout the US by Foundation members, with analyses performed by the Metropolitan Water District of Southern California (MWD) and Montgomery Watson Laboratories of Pasadena, California. These labs were among the first to utilize the new ion chromatographic method. MWD has periodically requested and received summaries of community and non-community data from the SCDHS.

In response to these and other findings, the *Interagency Perchlorate Steering Committee* (IPSC) was formed in early 1998. With members from the EPA and the DoD (the two co-chairs), the Agency for Toxic Substances and Disease Registry (ATSDR), and representatives of affected state and tribal governments, the IPSC acts as the clearing house for information, and serves to coordinate and focus resources in the areas of occurrence, detection, health affects assessment, characterization of exposure, treatment and contamination remediation. The IPSC is also responsible for determining research needs, and has a significant voice in the utilization of governmental resources in addressing those needs.

Monitoring Experiences in Suffolk County

SCWA, Westhampton

In the spring of 1998, responding to these previous perchlorate detection reports, monitoring in Suffolk County commenced with the voluntary collection of samples by the Suffolk County Water Authority (SCWA) from wells at five wellfields. The samples were sent to the Montgomery Watson Laboratory for analysis. Of the initial sample results one well – #3 at the Old Country Road wellfield in Westhampton – indicated a concentration of perchlorate of 30 ppb. Following notification to the Bureau of Drinking Water, a confirmation sample was collected, and the well was removed from service pending guidance from the New York State Department of Health (NYSDOH). The analysis of the confirmation sample indicated perchlorate at 23 ppb. Prior to its permanent retirement, this well later showed concentrations as high as 127 ppb in samples collected during subsequent test pumping.

The Westhampton site was selected by the SCWA for this initial sampling because of its past history as part of the former US Air Force BOMARC missile base. In subsequent months, the Bureau of Drinking Water consulted with the NYSDOH concerning an appropriate drinking water standard and analytical methodology, and made initial contact with IPSC members. Of particular importance were the initial discussions with EPA Region 9 staff involved in Superfund cleanup activities in the west, staff from the Metropolitan Water District of Southern California, and staff of the US Air Force (USAF). The Bureau began to address concerns relating to possible analytical interference from other substances. It also received information from the IPSC concerning users of perchlorate on Long Island and, through the USAF, obtained declassified information concerning the BOMARC missile program that showed that solid fuel BOMARC missiles had never been deployed at the Westhampton site. This confirmed observations made by staff of the Office of Pollution Control at the time of the deactivation of the BOMARC base which indicated that only liquid fueled missiles were deployed at the site. Both the Bureau and the USAF concluded that the perchlorate contamination of this SCWA well was unlikely to be related to the former deployment of liquid fueled BOMARC missiles at the site. With the BOMARC issue apparently resolved, attention turned to a review of more recent activities subsequent to the takeover of the BOMARC site by Suffolk County — specifically the Suffolk County Police Department (SCPD) practice of disposal of confiscated fireworks and munitions by burning. Between November 1998 and February 2000, a total of 18 profile wells were installed by the Bureau of Groundwater Resources in locations upgradient and downgradient of the fireworks disposal pit, which was located in the northwest corner of the site. Groundwater flow direction and water quality data appeared to eliminate other activities in the area as potential sources. Perchlorate was detected in 9 wells downgradient of the pit, in concentrations as high as 3,370 ppb. In November 1998, a meeting was held with staff from SCPD and the Office of the County Executive in which the results were reviewed, and modifications to the pit facilities were discussed.

The Suffolk County Water Authority filed a Notice of Claim against the county but the issue of legal responsibility remains unresolved. Late in 1998, the SCDHS issued a Request For Proposals for the engineering evaluation of possible alternatives for remedying the problem. Contract signing is expected early in 2001.

Other Monitoring Activities in Suffolk County

Throughout the summer of 1998, the SCWA worked on developing an in-house analytical capability at its own laboratory. It provided the Department with analyses of initial samples taken from the first SCDHS test well installed at the BOMARC site in September. By the beginning of 1999, methodology issues had resolved and all SCWA wells had been sampled repeatedly.

Initial State DOH concerns regarding the possibility of analytical interference in the analyses were satisfied by successive split and confirmatory sample analyses. By late fall 1998; the SCDHS Public and Environmental Health Laboratory (PEHL) had developed its own limited analytical capabilities. PEHL confirmatory analyses were able to show good correlation with SCWA results, and with those of an additional private lab (Agriculture and Priority Pollutants) and the US Air Force Research Lab at Wright-Patterson Air Force Base.

Then as now, limits on the number of samples the PEHL could analyze each month necessitated the prioritizing of monitoring objectives by the Bureaus of Drinking Water and Groundwater Resources. PEHL capacity has averaged about 30 samples a month, with analytical delays through much of 2000 attributed to PEHL staffing limitations and extraordinary equipment maintenance requirements. The primary Bureau of Drinking Water analytical priority in 1998-99 was to sample all community wells during the course of annual inspections, and to complete an initial monitoring of all non-community wells by mid-2000. This prioritization paralleled previous decision making when new analytical capabilities have been made available for survey purposes. The main objective of this prioritization was to provide a geographically balanced contaminant occurrence survey that focused on those water supply sources that affect the most people.

The data from the non-community wells were used in later decisions on the design of limited private well surveys, since non-community well construction and siting is fairly similar to those of private wells in the county. Historically, there has been a close correlation in contaminant occurrence between non-community supplies and private wells in the county. A competing resource demand from the Bureau of Groundwater Resources was to provide adequate PEHL analytical support for an ambitious study of the Westhampton BOMARC site, in which 109 samples were collected from the 18 profile wells installed beginning in the fall of 1998 through early 2000. Two small private well surveys were undertaken in 1998 – one in the vicinity of the BOMARC site, and the other near the Bellport site of the accidental Grucci fireworks factory fire in 1983. These were

relatively small commitments – a total of only 11 samples. Results indicated no perchlorate detection in either survey, most likely due to the locations of the wells relative to the potential source areas and, in the case of the Bellport site, the passage of time since the fire.

On the basis of the SCWA data and the initial PEHL analytical results, the Bureau required that all large public suppliers (serving populations greater than 10,000) conduct quarterly source water monitoring for a one year period. This began in 1999, in anticipation of the incorporation of perchlorate into the next Unregulated Contaminant Monitoring Rule, discussed later. The data from the 5 additional non-SCWA community suppliers further enhanced SCDHS annual inspection samples for the period, and confirmed SCDHS findings. West Coast contract laboratories, which are active in the analysis of perchlorate, were used to accomplish this special self-monitoring requirement.

To date, detectable perchlorate has been confirmed in a total of 36 community wells (6.8% of all community wells), located at 20 different wellfields, shown on Figure 1. Perchlorate has been detected in wells as deep as 609', further confirming its significant mobility in groundwater environments. Perchlorate has been detected in community wells in four towns in Suffolk County: Southold (13 wells at 8 wellfields), Brookhaven (4 wells, 3 wellfields), Southampton (6 wells, 2 wellfields), and Huntington (13 wells, 7 sites). In addition to Old Country Rd. Well #3 (at the former BOMARC site), one additional SCWA well (South Spur Dr. Well #2, East Northport) was voluntarily removed from service following one analytical result with a concentration at the State 18-ppb NYSDOH interim guideline. Concentrations often varied with the duration of pumpage, but the majority of wells with detection had concentrations no higher than 10 ppb. Other than the two restricted wells, only two others had maximum concentrations greater than 10 ppb, and these are located at the same two well sites as the restricted wells. For 21 wells, the majority of detections experienced were in the range of 3 to 7 ppb. Eleven of the wells show concentrations consistently at or below 5 ppb.

Perchlorate has been detected in 21 (4% of) non-community wells analyzed thus far, affecting 17 separate non-community supplies, shown on Figure 2. One non-community well at the Peconic Dunes County Park Nature Center indicated a concentration of 19 ppb and has been posted. With this exception, the remaining non-community detections were in the 3-8 ppb range.

The non-community perchlorate detections prompted additional private well surveys in Yaphank and Peconic. The Yaphank survey commenced due to the finding of low concentrations (7-8 ppb) in the Horseblock Road Shopping Center non-community supply. During the course of sampling 40 area wells from April to September 2000, perchlorate was detected in 11 private wells and was confirmed in one additional non-community supply. Three of the private wells exceeded the 18-ppb guidance limit, with concentrations between 24 and 26 ppb. These findings prompted a comprehensive investigation by the Bureau of Groundwater Resources and the Office of Pollution Control, which is discussed in detail in the SCDHS' report *Investigation Summary:*

Perchlorate Contamination in Yaphank, Suffolk County, NY. The test wells for this investigation required commitment of a significant portion of the PEHL's analytical capacity, with 122 samples collected from 20 wells from August through October of 2000. During 2001, the Bureau of Drinking Water expects to undertake a minimum of 9 additional private well surveys, while continuing surveillance monitoring of public water sources.

Discussion of Results

Although frequent and extensive analyses of community wells have been conducted, primarily by the SCWA, with confirmation by the SCDHS laboratory, the pattern of detection of perchlorate has been difficult to characterize, although an association with agricultural activities is implied.

The geographical distribution of non-detections of perchlorate however, may provide evidence that the problem in Suffolk is man-made. The lack of any detections in deep South Shore Magothy aquifer wells, which are generally free of man-made contaminants, may be an indicator that the presence of dissolved perchlorate ions found in other wells is not due to natural aquifer characteristics.

There is no consistent relationship between detections and agricultural activities. Samples collected by the Bureau of Drinking Water for this period indicate detectable pesticides or metabolites in 11 of these wells (see Bureau of Groundwater Resources: *Draft, Water Quality Monitoring Program To Detect Pesticide Contamination In Groundwaters of Nassau and Suffolk Counties, NY,* dated December 2000; *NYSDEC Water Quality Monitoring Program to Detect Pesticides in Groundwaters of Nassau and Suffolk Counties, Final Report,* dated June 1999). Conversely, there are many wells with a relatively long history of clear agricultural impacts- elevated nitrates and excessive pesticides- that have indicated no detectable perchlorate.

The possible relationship between fertilizer use and perchlorate detection came to light early in the SCDHS' evaluation of possible perchlorate sources. Bureau staff became aware of reports as old as 1896 noting the presence of perchlorate in Chilean nitrate fertilizer, varying from trace concentrations to 2.7%. Mineral beds called *caliche* are interspersed with deposits of gypsum, sodium chloride and other salts in many areas of South America, particularly Chile. Saltpeter (KNO_3), which is used in agriculture and the production of nitric acid, is also derived from the caliche beds. Anecdotally, the SCDHS has been advised that this fertilizer (Chilean nitrate), which is still commercially available, was the product of choice in many farm applications throughout Suffolk until generally replaced by cheaper ammonia-derived products in the late 1960s. However, the detection of perchlorate is not such that a direct relationship with older-source nitrate contamination is apparent in all cases. This may indicate current use of the Chilean product, but might support other studies indicating perchlorate is present in other agricultural products and non-agricultural products.

Prompted, in part, by the SCDHS' finding of perchlorate in agricultural areas, the Lockheed-Martin Corporation commissioned TRC to perform a study of agricultural products (*Chemical Fertilizer As A Potential Source Of Perchlorate,* unpublished, November 1998). This study indicated perchlorate in 5 of 8 products, including manufactured fertilizers, in amounts ranging between 0.75% and 2.7% by weight. In 1999, the USEPA Ecosystems Research Division conducted a second study (*Perchlorate Identification In Fertilizers,* Environmental Science and Technology, Volume 33, pages 3469-3472 and *Additions and Corrections,* Volume 34, page 224) finding between 0.6% and 0.84% in fertilizers, and between 0.1% and 3.64% in "fertilizer components," including phosphate rock, potash, ammonium phosphate, urea, langbenite, and Chilean nitrate. Langbenite ore, commonly mined in the Carlsbad area of New Mexico, is rich in potassium and magnesium sulfate compounds and is often used by organic farmers as a soil amendment to increase soil potash, magnesium, and sulfate content when soils are enhanced by animal manure or by "green manure" (a growing crop that is tilled into the ground). The Fertilizer Institute disputes both studies, and the EPA's researchers acknowledge inconsistencies in results for different lots of some of the same products (*Comment,* Environmental Science and Technology, Volume 34, pages 4452-4453). Nevertheless, these studies do serve to provide a possible explanation for at least some of the community and non-community detections found in Suffolk County.

A review of nitrate data for the community wells exhibiting perchlorate concentrations provides some insight into this discussion. Of these, 23 show nitrate concentrations consistently above 5 ppm. However, a number of these wells have contributing areas that have long been removed from agricultural use. This may suggest non-agricultural fertilizer use (residential nitrogen fertilizers). The aforementioned EPA agricultural fertilizer product study included 5 products apparently intended for home lawn care application, which had perchlorate from 0.15% to 0.84% by weight. Anticipated modeling under the Source Water Assessment Program should provide the necessary travel time and capture area information to clarify this issue.

Perchlorate has also been reported as a refining impurity in sodium chlorate. Sodium chlorate has many uses including as a herbicide. In response to a SCDHS query, Suffolk Cooperative Extension researched but did not find any reports of agricultural uses of sodium chlorate as a herbicide in the county. Sodium chlorate was ranked 14th, by weight, among the most extensively sold active pesticide ingredients on Long Island, according to the 1998 Pesticide Reporting Law data (*Environmental Advocates* report for 1998, on that organization's Internet site). However, reported commercial applicator (non-agricultural) usage weight was much lower, suggesting additional agricultural, and/or home applicator uses. This finding requires further investigation.

There is a clear need to evaluate the presence of low concentrations of perchlorate in other commercial–use chemical products, but a review of the literature alone may not provide adequate information. Material Safety Data Sheets (MSDS) are not required to identify any impurity present at less than 1% by weight.

Treatment Technologies

There is a pressing need to develop reliable treatment technologies that are able to reduce perchlorate concentrations in contaminated aquifer segments and in water supply sources, particularly in the areas of the country where significant water resources have been impacted or are threatened. The chemical properties of perchlorate, particularly its solubility and non-volatility, are such that traditional treatment methods, such as surface-water-style filtration, and granular activated carbon (GAC) or air stripping – the two processes utilized on Long Island for volatile organic chemical removal problems – have been shown to be ineffective. GAC treatment has been observed to remove perchlorate and nitrate only for very short periods of time. Additionally, on several occasions, perchlorate breakthrough (desorption) has been observed to produce, for short periods, effluent concentrations exceeding the influent concentrations.

Blending contaminated sources with uncontaminated supplies has been proven to be acceptable for a number of inorganic contaminants, and is utilized by the SCWA for a number of wells having elevated nitrate concentrations, several of which also have elevated perchlorate. Frequent SCWA monitoring is needed to ensure maintenance of acceptable blending ratios. However, a somewhat similar practice of "sweetening" wells (recharging treated water from the distribution system down the well casing during low demand periods for re-pumping during peak demand periods) may be less reliable, based on the SCWA's experience at South Spur Drive #2. Figure 3 indicates a dramatic change in perchlorate with pumpage during the summer of 1999, accompanied by nitrate increases of a somewhat slower rate over the same period.

Anion-exchange (IX) processes, utilizing ion exchange resins, have been shown to be effective, and in fact the SCWA's North Road nitrate removal IX plant in Southold has been shown to reduce perchlorate levels significantly. However other anions, such as chloride and sulfate, compete with the nitrate and perchlorate for resin removal capacity, reducing process efficiency. Frequent process control sampling is necessary to insure that the resins are regenerated prior to their failure. Additionally, regeneration is accomplished by brine addition – resulting in significant chemical use and waste disposal costs. Specific resins that may have better affinity for perchlorate have undergone tests, and at least one full-scale application of a Calgon ISEP resin has been funded.

Reverse osmosis has been proven to remove perchlorate in small-scale applications. Such small-scale units might prove effective in producing relatively small quantities of water in individual, single family applications, and is in common use in Suffolk in private well applications for point of use nitrate removal. It should be recognized that reverse osmosis applications would produce a small, but concentrated waste product of reject water. As a matter of policy, the SCDHS will always recommend the preferential alternative of connecting to a reliable public water supply, if available.

In groundwater plume remediation applications, anaerobic biochemical reduction has proven successful in both in-situ applications (chemicals and microbes introduced into the groundwater) and in more conventional bioreactor tank treatment plants. However, utilization of microbes has not been widely embraced in direct drinking water applications in the United States.

Projects amounting to several millions of dollars are currently committed to by federal and state agencies nationwide, as well as by the American Waterworks Research Foundation.

Health Issues

Data on the health effects of perchlorate, particularly those due to ingestion of low concentrations over a lifetime, are very limited. In 1992, the USEPA issued a Provisional Reference Dose (RfD), which is intended to provide an estimate of daily exposure by consumption that would not produce an adverse effect over a lifetime. The original EPA RfD, as well as a revision in 1995, was based upon evaluation of a study of potassium perchlorate that was conducted on Graves' Disease patients. Adjustments to the calculation of allowable lifetime exposure, called uncertainty factors, were applied to adjust for deficiencies in the data. The two provisional RfD values, applying two different uncertainty values, are the basis of most groundwater cleanup guidance values and drinking water standards that have been applied thus far by various states, including the 18-ppb Action Level currently in use in New York State.

The NYSDOH provisional standard for perchlorate requires Public Notification when perchlorate is found at 18 ppb, and requires large water suppliers to report findings in their Annual Water Supply Statements. The Action Level reflects the known effects of perchlorate on the thyroid relating to its medical use. Long-term human health effects studies on the consumption of small quantities of perchlorate have not been concluded. However, a number of animal studies are proceeding in an effort by the USEPA to provide this important information.

Future Actions

The USEPA placed perchlorate on its Contaminant Candidate List in 1998. Under the 1996 Amendments to the Safe Drinking Water Act (SDWA) EPA must, by 8/6/01, select at least five contaminants from the List and begin the process of formally regulating them, finalizing regulatory proposals by 8/6/03. However, the SDWA directs EPA only to select contaminants that have an adverse health effect, are known to occur at a frequency and at levels of health concern, and present a meaningful opportunity for health risk reduction while considering any sub-populations at a greater risk. Accordingly, in naming perchlorate to the List, EPA indicated research priorities in the area of analytical methodology, health research and occurrence. In an attempt to address questions concerning contaminant occurrence, EPA has included perchlorate on List 1 of the 1999

Final Unregulated Contaminant Monitoring Rule (UCMR). This will necessitate that those 3,493 public water suppliers in the United States which serve populations greater than 10,000 conduct a minimal monitoring effort for perchlorate over a three year monitoring period commencing in 2001. EPA's regulatory decision-making will be critical in determining the future allocation of federal resources in perchlorate research areas. In November 1999, EPA formally adopted Method 314.0, *Determination of Perchlorate in Drinking Water Using Ion Chromotography*, effectively embracing this analytical methodology for the UCMR occurrence study.

Continued SCDHS monitoring objectives are prioritized to confirm non-community detections, select and complete private well surveys, and continue independent community water supply source monitoring. To address lab capacity and analytical delays, the SCDHS proposed the purchase of an additional ion-chromatograph in the recent NYSDOH-approved work plan for the Drinking Water Enhancement Program. Funds are expected in the first quarter of 2001. Increased frequency of testing of private wells for perchlorate should help to clarify the magnitude of occurrence in agricultural areas. This in turn, along with application of the county's Groundwater Model, should address this emerging issue in the upcoming Source Water Assessment Program (SWAP) for public water supplies.

Through the Interagency Perchlorate Steering Committee, there should be additional emphasis on continued research into the presence of perchlorate at trace levels in other common-use chemical products. The SCDHS should remain in close contact with the IPSC, particularly as studies evaluating human health risk continue. As needed, the SCDHS' Bureau of Drinking Water will work closely with IPSC and the NYSDOH to realistically evaluate exposure and to provide necessary analytical studies for decision making. In addition, the SCDHS should continue cooperating with the NYSDOH in a statewide perchlorate survey, with sample analysis to be completed by the state's Wadsworth Laboratory.

Figure 1

Community Public Supply Wells
Suffolk County, New York
1999/2000 Perchlorate Results

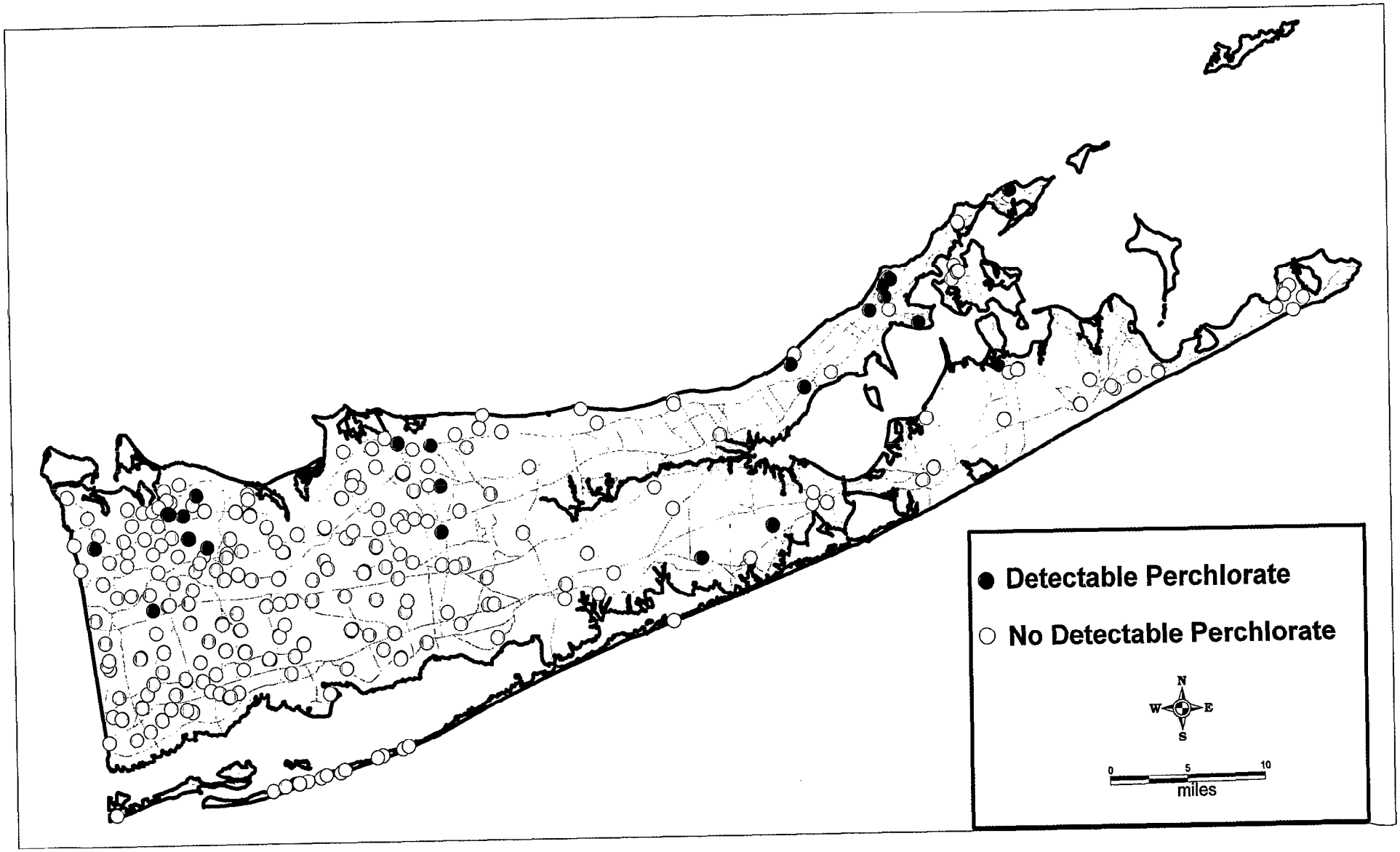

Figure 2

Non-Community Public Supply Wells
Suffolk County, New York
1999/2000 Perchlorate Results

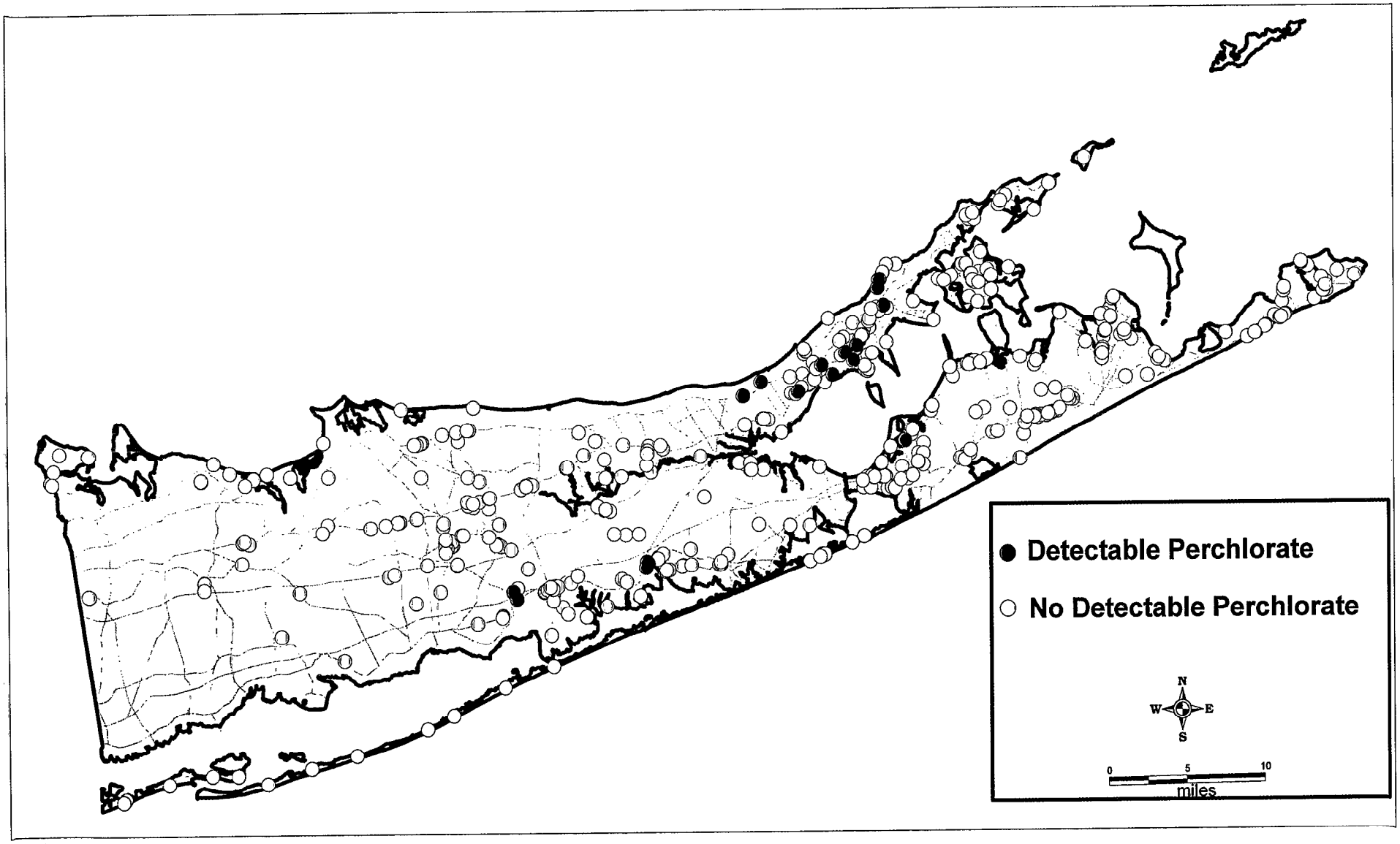

Figure 3
SCWA Perchlorate & Nitrate Data
South Spur Drive #2
January - November 1999